

4 Conclusions

This chapter presents conclusions that integrate findings outlined in the previous chapter.

Conclusion #1: The ozone weekend effect is real

Careful statistical analyses of the available data demonstrate that the ozone weekend effect is a persistent reality and not just a transient condition or false impression.

Ozone measurements in some locations are typically higher on weekends, particularly on Sunday, compared to weekdays. On the other hand, ambient concentrations of VOCs and NO_x, the major smog-forming pollutants, are typically lower on weekends almost everywhere, based on available air quality data and source-activity data, such as traffic counts.

Lower concentrations of ozone precursors on weekends seems reasonable because these emissions come from sources, such as cars, trucks, power plants, refineries, and factories, that intuition may expect to be less active overall on weekends compared to weekdays. Although it is likely that the major sources decrease in activity, some other activities, such as home maintenance, recreation, and shopping trips, may increase on weekends. On Saturday in some locations, for example, the total volume of mid-day traffic on freeways can be greater than on weekdays.

Characteristic differences between weekend ozone and Friday ozone are the following for four California air basins using data for 1996 – 1998:

- South Coast Air Basin – 22 ppb or 30% higher than Friday ozone
- San Francisco Bay Area Air Basin – 9 ppb or 25% higher than Friday ozone
- Sacramento Metropolitan area – 5 ppb or 8% higher than Friday ozone (not statistically significant)
- San Joaquin Valley Air Basin – 4 ppb or 6% higher than Friday ozone (not statistically significant)

Conclusion #2: A combination of VOC and NO_x reductions has been highly successful at reducing ambient ozone levels on all days of the week everywhere in the basin for more than 20 years in the South Coast Air Basin. Nevertheless, the ozone weekend effect occurs throughout the SoCAB.

In the late 1990s, the ozone weekend effect was observed at all locations in the South Coast Air Basin for which data were analyzed (see Section 1.4 of the TSD).

From the mid-1970s into the 21st century, the ozone control strategy implemented in the SoCAB included reductions of both VOC emissions and NO_x emissions. Early NO_x reductions were achieved by statewide controls on emissions from motor vehicles combined with local controls on emissions from industrial sources, such as cement kilns and power plants.

While both VOC and NO_x emissions decreased substantially, ambient ozone levels also declined substantially on all days of the week at all locations in the basin (See Section 1.1 of the TSD).

Conclusion #3: The ozone weekend effect does not invalidate NO_x reductions as an important ozone control strategy. In addition, NO_x reductions are almost certainly beneficial in reducing concentrations of some other pollutants, such as, PM-nitrates, nitrogen dioxide, and PAN.

The ozone weekend effect is not a simple phenomenon, and may be caused by any of several processes operating separately or in concert. The causes of the ozone weekend effect might persist during periods when NO_x reductions cause ozone concentrations to improve on all days of the week. Until the causes of the ozone weekend effect are determined satisfactorily, NO_x reductions remain a rational and valid element of ozone control strategies in California.

In addition, NO_x reductions affect pollutants other than ozone. Ambient concentrations of peroxyacetylnitrates (PAN) and nitrogen dioxide (NO₂) are affected by NO_x emissions. PAN irritates nasal and lung passages but does not have an air quality standard established for it. Recent research on health effects indicates that exposure to air pollutants for multiple years lowers the growth rate of lungs in children. The pollutants most strongly associated with this effect include NO₂, particulate matter, and nitric acid. Air quality standards for NO₂ were attained relatively recently in the South Coast Air Basin.

Reductions in NO_x emissions can also reduce the mass of nitrate particles in the air. Particulate nitrates often make up a large fraction of the total mass of PM_{2.5}, which can penetrate deeply into lungs. Most particulate nitrates are formed, in part, from gaseous NO_x emissions through photochemical processes.

Because multiple pollutants are affected by NO_x reductions, they are often considered together, rather than separately, when developing pollution control plans.

Conclusion #4: Ambient concentrations of particulate matter tend to be lower on weekends compared to weekdays.

Particulate matter (PM) in the air we breathe is a significant health concern. Exposure to particle pollution is linked to increases in the frequency and severity of asthma attacks and bronchitis. Even premature death in people with cardiac or respiratory disease has been attributed to elevated PM concentrations in the ambient air. Populations sensitive to particle pollution include people with respiratory or cardiac problems, children, and the elderly. Prolonged and repeated exposure can also have adverse impacts. All particles can be harmful when inhaled, whether “coarse” (2.5 to 10 microns in aerodynamic diameter) or “fine” (less than 2.5 microns in aerodynamic diameter).

Analysis of PM concentrations indicates a general weekly pattern with the maximum occurring late in the workweek and the minimum occurring on weekends (especially Sunday); however, the pattern is not statistically significant in some locations.

Many different sources contribute to PM. Some sources emit PM directly (primary particles) while other sources emit pollutants that form secondary particles as they react in the atmosphere. Meteorological conditions can also affect PM concentrations strongly. Therefore, the cause(s) of day-of-week differences in PM concentrations are difficult to determine with confidence.

Ammonium nitrate – a secondary product of NO_x and ammonia emissions – is generally the largest contributor to $\text{PM}_{2.5}$ concentrations during the winter at many urban sites in California and is also significant during the summer months in the SoCAB. Several studies indicate that ammonium nitrate can account for over half of the $\text{PM}_{2.5}$ mass during episodes with elevated particle levels in California. Understanding how particulate ammonium nitrate is formed and how to effectively reduce it through controls on sources of NO_x , ammonia, or other pollutants influencing its formation is a critical component in the development of California’s $\text{PM}_{2.5}$ program.

A factor contributing to increased $\text{PM}_{2.5}$ concentrations in the winter is meteorology that favors the formation of secondary nitrate and sulfate. Cool temperatures, low wind speeds, low inversion layers, and high humidity are conditions that can lead to high concentrations of these particles. These meteorological conditions can also occur in marine layers during the summer.

The formation of secondary particles from precursors is a complex, nonlinear process, and one should not expect to see one-to-one relationships between precursor emissions and ambient concentrations of secondary PM.

Chemical reactions in the atmosphere convert NO_x emissions into very small nitrate particles. On weekends, activities that produce NO_x emissions

appear to be substantially reduced. For example, heavy-duty diesel trucks are much less active on weekends than weekdays. Not surprisingly, average weekend concentrations for particulate nitrates tend to be lower than the average weekday concentrations.

Conclusion #5: Ambient concentrations of some important TACs (toxic air contaminants) tend to decrease on weekends compared to weekdays

During the 1990s, ambient concentrations of two important carcinogens – benzene and 1,3-butadiene – decreased substantially. For example, between 1990 and 1998, the annual average concentration of benzene measured at Burbank, CA, declined by approximately 65 percent. The decrease in concentrations of 1,3-butadiene is also substantial, though somewhat smaller.

At the same time, ambient concentrations of these and other important TACs did not increase on weekends in areas where ozone concentrations do increase on weekends. In most cases, weekend concentrations were lower than weekday concentrations. This “negative” weekend effect appears to hold for primary TACs, such as benzene; 1,3-butadiene; and perchloroethylene, as well as secondary TACs, such as formaldehyde and acetaldehyde.

Particles contained in smoke from diesel engines have been identified as an important TAC. Ambient concentrations of elemental carbon (EC) include the particles from diesel smoke. Limited analysis of air quality data indicates that EC concentrations are probably lower on weekends compared to weekdays. This would be consistent with traffic data indicating that heavy-duty diesel trucks are much less active on weekends compared to weekdays.

Conclusion #6: Several processes may contribute to the ozone weekend effect. The relative importance of these processes cannot be resolved with presently available data from field studies, laboratory experiments, and modeling exercises.

The analyses in this report provide a significantly better understanding of the ozone weekend effect. Still, the evidence falls short of determining the cause or causes of the ozone weekend effect. Of the six hypotheses in Chapter 3, at least four are plausible and may explain a significant portion of the ozone weekend effect. Crucial gaps in the available data preclude a final judgement concerning the relative importance of the plausible causes of the ozone weekend effect.

The research required to close the gaps in the data includes field studies, laboratory experiments, modeling exercises, and well-conducted analyses of all the resulting data. None of these areas of research would be sufficient by

itself. Although the necessary work will require a multi-year effort, reliable determinations depend on significantly expanded and improved databases.

The data available today permit only a general assessment of the plausibility of the hypotheses in Chapter 3.

Conclusion #6a: The “NO_x-reduction” hypothesis is plausible but not proven.

The following observations are relevant to this conclusion:

- VOC/NO_x ratios measured at the surface in the SoCAB during daylight hours on all days of the week are generally in the “VOC-limited” range (less than 8 to 10).
- VOC/NO_x ratios during daylight hours on weekends are generally 10-20% higher on Saturdays and 20-40% higher on Sundays compared to weekdays.
- NO₂ to NO ratios on weekends are higher than on weekdays during daylight hours.

Limitations in the data pertinent to this conclusion are the following:

Directly measured VOC data are available for only a few locations in the SoCAB. An hourly database of accurate VOC measurements representing all parts of a region for all days of the week (with adequate replication) is not available anywhere in California, perhaps anywhere in the world.

The precision of air quality measurements is often too coarse to see significant changes in the VOC/NO_x ratio. Routine VOC measurements from the PAMS program may significantly underestimate the true VOC concentrations, while routine NO_x measurements systematically overestimate the true sum of NO and NO₂ due to artifacts included in the data. Therefore, the true VOC/NO_x ratios may be substantially higher (20-40% or more) than the VOC/NO_x ratios based on ambient data.

For all days, ambient NO_x concentrations are usually under 60 ppb by mid-day and rarely exceed 60 ppb at any time on Sunday. Such “low NO_x” conditions may significantly reduce the ozone-forming potential of VOCs.

Accurate, artifact-free measurements of VOC species and NO_x species (NO, NO₂, and other important nitrogenous pollutants) are needed. Besides surface measurements, these data are needed at several altitudes above the ground to help separate the contributions of the “NO_x-reduction” hypothesis, the “NO_x-timing” hypothesis, and the “carryover aloft” hypothesis.

Conclusion #6b: The “NO_x-timing” hypothesis is plausible but not proven.

The following observations are relevant to this conclusion:

- Measured VOC/NO_x ratios during daylight hours on weekdays and weekends are generally in the “VOC-limited” range (less than 8 to 10), but increase, becoming less “VOC-limited,” as the hours progress.
- NO₂ to NO ratios on weekends are higher than on weekdays, especially in the early daylight hours, indicating more active photochemistry.
- Ozone concentrations increase more rapidly on weekends than weekdays.
- NO_x concentrations on weekend mornings are typically 40-50% of the concentrations on weekday mornings. By the early afternoon, however, weekend NO_x concentrations are only 60-80% of weekday levels, indicating that NO_x concentrations are “catching up” to weekday levels.
- Due to dilution and to chemical reactions, ambient NO_x concentrations are in the “low NO_x” range (<100 ppb) before mid-day almost everywhere, especially on Sunday. Though the VOC/NO_x ratio may be in the “VOC-limited” range, the low NO_x conditions may cause mid-day NO_x emissions to promote rather than inhibit ozone formation.

Limitations in the data pertinent to this conclusion are the following:

Additional field sampling and chemical analyses are needed, along with modeling to ascertain how different the photochemical state of the atmosphere is on weekends compared to weekdays.

Accurate, artifact-free measurements of VOC species and NO_x species (NO, NO₂, and in three dimensions are needed to assess the contributions of the “NO_x-reduction” hypothesis, the “NO_x-timing” hypothesis, and the “Carryover aloft” hypothesis. [Repeated in Conclusion 10 below.]

Conclusion #6c: The “carryover near the surface” hypothesis is plausible but not likely to be an important factor.

Carryover within the nighttime layer of cool air near the surface is probably not an important factor contributing to the ozone weekend effect. Traffic activity data on freeways in the South Coast Air Basin indicate greater activity on Friday and Saturday evenings. However, air quality data indicate that ambient concentrations of VOCs and NO_x from sunrise on are lower on weekends compared to weekdays.

The following observations are relevant to this conclusion:

- Total traffic on Friday and Saturday nights is greater than the total traffic on other nights.
- Ambient concentrations of CO and NO_x during the nighttime hours on Friday and Saturday nights are similar to or higher than the nighttime concentrations on other days of the week.
- Ambient concentrations of CO and NO_x during the early daylight hours on Saturday and Sunday are similar to or lower than the comparable concentrations on weekdays.

Limitations in the data pertinent to this conclusion are the following:

However, because VOC data have historically been limited in quantity and quality, analysis of more good quality (e.g., better precision and accuracy) data is needed to confirm this for hydrocarbon concentrations. The fate of ozone precursor emissions during the night needs to be confirmed whether or not the reaction products can become photochemically active when the sun rises.

Conclusion #6d: The “carryover aloft” hypothesis is plausible but not proven.

The following observations are relevant to this conclusion:

- Based on measurements with LIDAR, airplanes, and balloons, reservoirs of ozone and ozone precursors appear to occur aloft frequently, perhaps routinely, in the South Coast Air Basin.
- Reservoirs aloft are frequently substantial, some being thousands of feet thick beginning a few hundred feet above the surface, and containing 60 – 140 ppb or more of ozone.
- Measurements aloft indicate that photochemistry is frequently NO_x-limited or NO_x-sensitive. Concurrent surface measurements usually indicate the reverse.
- LIDAR data and three-dimensional dispersion models indicate that pollutants aloft generally begin mixing into the nocturnal boundary layer three or more hours before the ozone maximum occurs.
- Some LIDAR data indicate that pollutants sequestered aloft may generate additional ozone before mixing begins with fresh emissions from the surface.

Limitations in the data pertinent to this conclusion are the following:

Measurements of air quality aloft are typically made during special field studies on days when high ozone concentrations are anticipated. Air quality measurements aloft, especially of ozone and ozone precursors, are needed on many more days, including non-episode days. These measurements are needed for weekday-weekend transitions (Fri. to Sat. to Sun. to Mon.). In addition, photochemical modeling that replicates the observed carryover phenomena is needed to evaluate the influence of carryover aloft on the ozone weekend effect.

Accurate, artifact-free measurements of VOCs and NO_x in three dimensions are needed to assess the contributions of the “NO_x-reduction” hypothesis, the “NO_x-timing” hypothesis, and the “Carryover aloft” hypothesis. [Repeated from Conclusion 8 above.]

Conclusion #6e: The “increased weekend emissions” hypothesis is not plausible.

According to the increased weekend emissions hypothesis, total smog-forming emissions increase on weekends. A few observations are consistent with this hypothesis, but the vast majority of air quality data does not support it.

The following observations are relevant to this conclusion:

- The Lynwood monitoring site represents a large urban source region for VOCs and NO_x. This site records the highest mid-day levels of CO on Saturdays (10 a.m. to 3 p.m.). However, this observation should not be generalized in support of the increased weekend emissions hypothesis for two reasons. First, the highest ozone day in the SoCAB is Sunday, rather than Saturday. On Sunday, Lynwood CO levels do not exceed mid-week levels between 6 a.m. and 8 p.m. Second, no location other than Lynwood shows a similar pattern.
- Daily total vehicle counts at some Weigh-in-Motion stations in the SoCAB are higher on some weekend days than on weekdays. However, these stations tend to be at peripheral locations affected by traffic leaving and entering the basin.
- Hourly vehicle counts from 11 a.m. through 3 p.m. are often higher on Saturday than on weekdays. However, mid-day vehicle counts on Sundays at almost all locations are lower than on weekdays, and Sundays have the highest ozone everywhere in the SoCAB.
- Air quality data at most locations do not support the Increased Weekend Emissions Hypothesis. With the exception of CO on

Saturdays at the Lynwood and El Toro monitoring sites, ambient measurements of CO (partial hydrocarbon surrogate) and NO_x are lower on weekends compared to weekdays for all daylight hours.

Conclusion #6f: The “soot and sunlight” hypothesis is plausible (theoretically) but not proven.

According to the “soot and sunlight” hypothesis, concentrations of particles that absorb ultraviolet sunlight are lower on weekends compared to weekdays. Therefore, more ultraviolet sunlight is available to drive ozone-forming reactions in the atmosphere, and this causes ozone concentrations on weekends to be greater compared to weekdays.

At this time, only a few theoretical exercises and a limited store of field measurements are available to support this hypothesis. The recommendations in this report include steps to acquire the data needed to evaluate this hypothesis more fully.

Conclusion #7: A coordinated research program including field studies, laboratory experiments, and modeling exercises can provide a realistic hope of resolving the cause or causes of the ozone weekend effect.

The cause or causes of the ozone weekend effect are difficult to resolve with existing data. As discussed under Conclusion #6, crucial gaps in the available data preclude a final judgement concerning the relative importance of the plausible causes of the ozone weekend effect.

The research needed to determine the cause(s) of the ozone weekend effect includes field studies, laboratory experiments, modeling exercises, and well-conducted analyses of all the resulting data. None of these areas of research would be sufficient by itself.

The recommendations in the following chapter outline a research program that may provide the crucial data needed to fill the important gaps. Although the necessary work will require a multi-year effort, reliable conclusions depend on significantly expanded and improved databases. The issues are reasonably clear, and the answers are within reach.

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